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Ammonia Borane and Sodium Borohydride: Boron Hydrides as Hydrogen Storage Materials Intended to Specific and Different Applications

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1 Introduction

Hydrogen storage is still today one of the most significant issues hindering the development of a 'hydrogen energy economy'. It is a significant challenge and to take up it several solutions, based on either physisorption of H_2 or chemisorption of H, have been considered up to now [1]:

- Physical storage: i.e. compressed H_2, liquid H_2, (cryo-)adsorption in adsorbents such as zeolites;
- Chemical storage: i.e. hydrolytic hydrides (e.g. sodium borohydride $NaBH_4$ (SB)), metal hydrides (e.g. MgH_2), complex hydrides (e.g. sodium alanate $NaAlH_4$), amine-borane adducts (e.g. ammonia borane NH_3BH_3 (AB)), amides/imides, hydrocarbons, glass microspheres, ice hydrates.

From all of these possibilities, hydrolytic hydrides and amine-borane adducts are noticeable by their high hydrogen densities[1]. For example, the 2000s have seen the emergence of, first, SB and, then, of AB, which are constituted of 10.8 and 19.5 wt% of hydrogen respectively [2].

As noticed by Eberle et al. [1], "storage of hydrogen is a substantial challenge, especially for applications in vehicles" and the automotive industry is the eagerest in expecting an efficient storage solution. Accordingly the U.S. Department of Energy (US DOE) has set quite severe application targets [3]. For example, one of the most known targets, which is also one of the most used to discuss the potential of a storage solution, is the gravimetric hydrogen storage capacity [2]. Even though the GHSC targets have been recently revised downwards, meeting them is a significant challenge. For example, the US DOE recommended a no-go for SB for automotive applications in 2007 because of too low eHDs and therefore too low GHSCs [4]. Nevertheless $NaBH_4$ still has a potential for portable [5] and niche fuel cell applications [6]. While recommending the no-go for SB, the US DOE strongly suggested intensifying the efforts devoted to AB while valorizing the know-how on SB.

For both SB and AB, one of the main challenges is to release efficiently the maximum of the stored hydrogen. To succeed in that, several dehydrogenation routes (Figure 1) have been considered so far: the SB hydrolysis [7] and methanolysis [8]; and the AB hydrolysis [9],

[1] In accordance with the definitions set by the US DOE, the term "gravimetric hydrogen storage capacity" (denoted GHSC) will only be used for a complete storage system (including the tank, storage media, safety system, valves, regulators, piping, and so on). The term "theoretical hydrogen density" (denoted HD) will define the gravimetric content of hydrogen in the storage media (e.g. SB or AB). The term "effective hydrogen density" (denoted eHD) will refer to the content of hydrogen really released from the storage media.

methanolysis [10] and thermolysis [11]. Note that thermolysis of SB needs too high temperatures, even in the presence of a catalyst, to be considered suitable for applications (i.e. T > 400 °C) [3]. With respect to the solvolysis reactions (with liquid water and methanol), the HDs of the systems $NaBH_4$-$2H_2O$, $NaBH_4$-$4CH_3OH$, NH_3BH_3-$2H_2O$ and NH_3BH_3-$4CH_3OH$ are 10.8, 4.8, 9.0 and 3.8 wt%, respectively (Figure 1). However these theoretical values (taking into account only the stoichiometric amount of solvolytic agent) are difficulty achieved because of some problems: e.g. excess of the solvolytic agent that is used also as solvent, formation of thermodynamically stable borate hydrates, limited solubility of the hydrogen storage materials as well as that of the borates, weight of the by-products, and volume expansion (borates/SB or borates/AB, %). Today the yield of the H_2 release is not an issue anymore as very reactive catalysts have showed to convert 100 % of SB or AB with variable hydrogen generation rates (HGRs). The issue with the catalytic materials is rather durability [8].

Hydrolysis @ <85°C	
$NaBH_4 + 2\ H_2O \rightarrow NaBH_2 + 4\ H_2$	10.8 wt%
$NH_3BH_3 + 2\ H_2O \rightarrow NH_4BO_2 + 3\ H_2$	9.0 wt%
Methanolysis @ <85°C	
$NaBH_4 + 4\ CH_3OH \rightarrow NaB(OCH_3)_4 + 4\ H_2$	4.8 wt%
$NH_3BH_3 + 4\ CH_3OH \rightarrow NH_4B(OCH_3)_4 + 3\ H_2$	3.8 wt%

Thermolysis @ 120-500°C	
$NaBH_4$ *not considered*	
$n\ NH_3BH_3 \rightarrow [NH_2BH_2]_n + H_2$	6.5 wt%
$[NH_2BH_2]_n \rightarrow [NHBH]_n + H_2$	6.5 wt%
$[NHBH]_n \rightarrow [NB]_n + H_2$	6.5 wt%
$n\ NH_3BH_3 \rightarrow [NB]_n + 3\ H_2$	19.5 wt%

Figure 1: Ideal solvolysis of SB and AB and thermolysis of AB.

We are currently much involved in the solvolysis of SB and AB and we are working especially on the development of reactive, durable metal-based (mainly Co) catalysts as well as on optimizing the eHDs of the systems specified above. Hereafter are reported our main results concerning both topics. In a last section entitled ‘outlook and conclusion’, the AB thermolysis is briefly considered as it appears to be the most promising route for the automotive applications despite storage irreversibility.

2 Short Survey About the Metal Catalysts in the Solvolysis of SB and AB

With respect to the hydrolysis of SB, a great number of studies have been published since the late 1990s and the Amendola et al.’s pioneer work [12]. Most of them are about catalytic materials. Liquid or solid acids [13, 14], metal salts in solution [14] or loaded into solid SB [15], metals [16], metal borides [17], metal alloys [18] and supported metals (mainly Ru or Co) [19, 20, 21, 22] have been considered. Highly reactive catalysts that are mainly based on Co have often been reported and, frankly speaking, preparing such catalysts is not an issue anymore. We have investigated acids such as acetic acid [15] and metal-based catalysts such as cobalt [16] and aluminum [23] salts, cobalt fluorides and borides [24], and Ru or Co supported catalysts [20, 25], and the main conclusion of our works is that variable hydrogen generation rates with total conversions of almost 100 % can be easily obtained with various types of catalysts. This is illustrated by the data listed in Figure 2. Note that the conclusion given above holds also to the SB methanolysis.

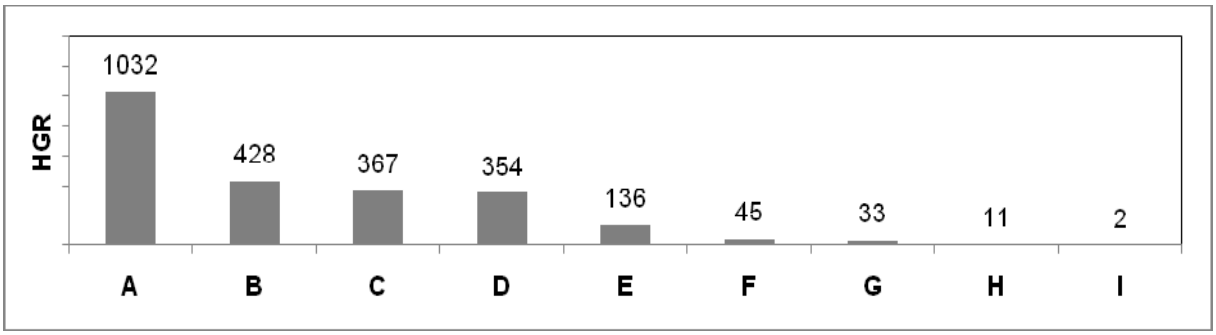

Figure 2: Hydrogen generation rates (L min^{-1} g^{-1}(metal)) for some metal-based heterogeneous catalysts at ambient conditions: A: $RuCl_3$-$AlCl_3$ [24]; B: 10 wt% Ru-LiCoO2 [21]; C: 15 wt% Pt-$LiCoO_2$ [22]; D: $AlCl_3$ [21]; E: 10 wt% Co-C [24]; F: $CoCl_2$-Al_2O_3 [26]; G: Co [25]; H: 1 wt% Ru-ZrO_2-SO_4^{2-} [20]; I: $CoCl_2$ [16].

Regarding the AB hydrolysis, the first published studies date back the middle of the 2000s. Xu's group may be considered as the leader group in this area [26]. Similarly to SB, most of the works focused on the reactivity of the developed metal-based (heterogeneous [10] and homogeneous [27]) catalysts. For example, the following hydrogen generation rates have been reported to occur at ambient conditions: e.g. 10 mL min^{-1} for Pt-Ru/C at 20 °C [28], 12 mL min^{-1} for 1 wt% Rh/TiO_2 at 40 °C [29], 25 mL min^{-1} for Rh^0 nanoclusters at 35 °C [28], 67 mL min^{-1} for Co-Mo-Fe/Ni foam at 25 °C [30], 100 mL min^{-1} for Pd^0 nanoclusters at 25 °C [31] and 140 mL min^{-1} for Ru^0 [32]. Recently we have reported a hydrogen generation rate of 21 mL min^{-1} for $CoCl_2$ [33]. Hydrogen generation rates > 600 mL min^{-1} for Ru-based catalysts have even been achieved at 40 °C. However that may be, similarly to SB it is not so problematic to synthesize reactive catalytic material for hydrolyzing AB.

In fact, the main problem with the metal catalysts used in the hydrolysis of both SB and AB is their limited durability. Agglomeration of particles, surface oxidation and component dissolution in alkaline SB solutions are common reasons for catalysis deterioration of a catalyst [8]. Synthesizing stable catalysts is one of our concerns. For example, in a previous study it was considered fluorination of Co nanoparticles in order to prevent them from oxidation or boronation [25]. In this case, the catalyst was in powder form and this is another problem. Handling of powder catalyst is not easy and above all it is not convenient for start-and-stop applications, that's why we are also working on shaped catalysts, which are evidently much more practical. Our criteria of success are as follows: shaped catalysts as reactive as powder catalysts; and durable shaped catalysts that will permit start-and-stops without reactivity degradation, which is important since in practical uses support failure of the catalyst support and catalyst erosion are reasons to the catalyst deterioration due to mechanical constraints of the generated hydrogen bubbles and flushing of the SB or AB solution [8]. Accordingly, we are working on developing 2D shaped catalysts consisting of Co^0 or supported Co catalysts deposited over Ni foam by electrodeposition or electroless deposition, over polymeric films by electrodeposition, and over Cu/stainless steel plates by electrophoretic deposition (Figure 3). Our preliminary results show that for optimized shaped catalysts high reactivity, even higher than that of equivalent catalysts in powder form, and relative durability can be achieved.

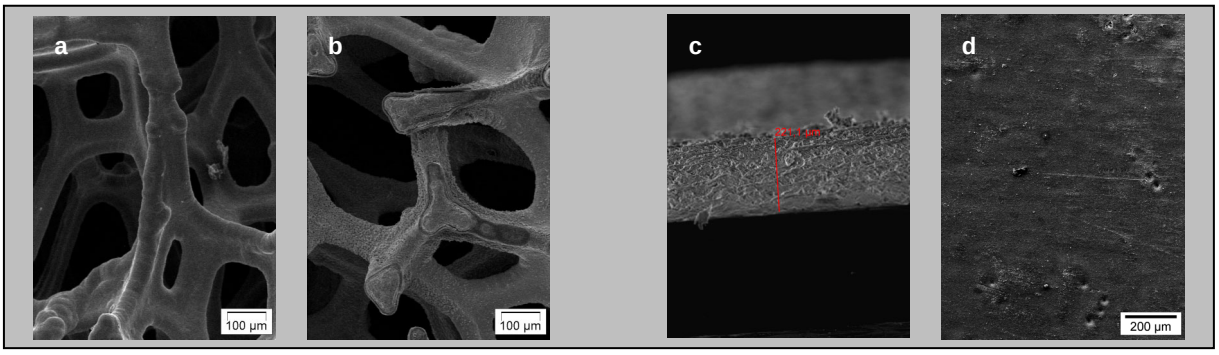

Figure 3: SEM images of (a) Ni foam, (b) Co-Ni foam, (c) and (d) Co-Al_2O_3-Cu thickness and surface.

3 Effective hydrogen Densities

Recently, we concluded that "none of both boron hydrides is mature enough to envisaging applications, especially automotive applications, both suffering from low, but not-optimised, effective hydrogen storage capacities" [3]. It was for example showed that to date the highest effective GHSCs are 4.5 and 2.5 wt% for the systems $NaBH_4$-H_2O and NH_3BH_3-H_2O, respectively. The question that is then asked is: may SB and AB be envisaged for automotive applications when their hydrolysis is considered? For the former hydride, the answer was given by the US DOE when a no-go was recommended [5]. With respect to the latter compound, the answer is quite evident. Given that the HD of NH_3BH_3-$2H_2O$ is only of 9.0 wt%, the highest GHSC that could be obtained is 4.5 wt%[2], that is, far from the targets for automotive applications by 2015 [4]. However portable applications can still be considered even if there is no target clearly set [3].

In the hydrolysis of SB, several issues make reaching the HDs given in Figure 1 difficult. Actually the hydrolysis takes place in an excess of water owing to two reasons. The 1st reason is that the thermodynamically stable form of the borate by-products is the hydrated one, namely $NaBO_2.xH_2O$:

$$NaBH_4 + (2+x)\ H_2O \rightarrow NaBO_2.xH_2O + 4\ H_2$$

For example, Marrero et al. [34] particularly showed that $NaBO_2.2H_2O$ predominates over $NaBO_2.4H_2O$ at ambient conditions. Accordingly the HDs of SB-(2+2)H_2O and SB-(2+4)H_2O are only of 7.3 and 5.5 wt%, respectively. It is noteworthy that this can also be applied to the AB hydrolysis even though as far as we know no study about its by-products has been reported yet:

$$NH_3BH_3 + (2+x)\ H_2O \rightarrow NH_4BO_2.xH_2O + 3\ H_2$$

[2] Assuming that the AB weight is 50 % of the weight of the complete storage system.

The HDs of AB-(2+2)H_2O and AB-(2+4)H_2O will then be of 5.8 and 4.3 wt%. To get round such a problem, it has been suggested to methanolyze SB or AB as $B(OCH_3)_4^-$ is not hydrated in ambient conditions. This has been confirmed through our works as we showed, by XRD and IR, the formation of only $NaB(OCH_3)_4$ through the hydrolysis of SB [35]:

$$NaBH_4 + (4+x)\ CH_3OH \rightarrow NaB(OCH_3)_4 + 4\ H_2 + x\ CH_3OH$$

The 2nd reason of using an excess of solvolysis agent is that both SB and AB as well as the respective by-products have a limited solubility. For example, the solubility of SB, AB and $NaBO_2$ in water are 55, 28 and 34 g per 100 g(H_2O). Actually the limited solubility is problematic to the catalytic material since any by-product precipitation may be detrimental to its reactivity. These last years, the utilization of SB or AB in a solid state [34, 37, 36] has discarded such an issue as for portable applications it is more and more often considered a single use of the catalyst, the catalyst likely deactivation being then unimportant.

The HDs given in Figure 1 are theoretical and the eHDs can be at best equal to the HDs[3]. Accordingly we carried out a series of experiments in order to determine the eHDs that can be achieved in our experimental conditions and in the presence of a Co catalyst. Typically we followed the solvolysis of SB or AB by injecting various amounts of water in accordance with the hydrolysis equations given above and with *x* varying from 0 to 8. The SB/AB total conversion (TC, %) was determined and the eHDs were calculated as (TC×HD)÷100. Figure 4 shows the results we obtained, which can be summarized as follows:

- SB-(2+*x*)H_2O: the highest eHD, i.e. 7.3 wt%, is obtained for *x* = 2, the TC being 100 %;
- SB-(4+*x*)CH_3OH: the highest eHD, i.e. 3.4 wt%, is obtained for both *x* = 0, the TC being 74 %, and *x* = 2, the TC being 100 % [37];
- AB-(2+*x*)H_2O: the highest eHD, i.e. 7.8 wt%, is obtained for *x* = 0, the TC being 96 % [34];

In every case the catalyst weight was taken into account for the eHD calculations. It is noteworthy that the by-products precipitated for the small *x* values (i.e. *x* = 0-4). To summarize, eHDs of 7-8 wt% can be achieved with SB or AB, suggesting therefore GHSCs up to 4 wt% [35].

When SB is envisaged to be stored as a solid, there is another problem that reduces the eHDs. The problem is the volume expansion since the borates volume is larger than the volume of solid SB [37]. For example, a volume expansion of 173 and 197% has been reported elsewhere [38, 39]. We studied the volume expansion for SB and AB. As $NaBO_2.2H_2O$ is the predominating borate, the volume expansion at 20 °C and in the presence of a Co-catalyst (10 wt% of $NaBH_4$+Co) was determined for *x* = 2. It was found to be 156 %, which is consistent with the values reported above (while considering the Co presence). With respect to AB, no volume expansion was noticed. Surprisingly, for *x* = 2, it

[3] It can be considered to use steam from a fuel cell in order to hydrolyze SB or AB. By this way, the respective HDs are 21.1 and 19.5 wt% (the 2 water molecules are not taken into account in the calculation of the HD). However, such an approach is not considered here as in our opinion this is only feasible for the automotive applications.

was found a volume regression of 50 %. Hence, with SB the tank must be 64%-filled (the amount of stored hydrogen will then be 64%-lower) whereas with AB the tank can be 100%-filled.

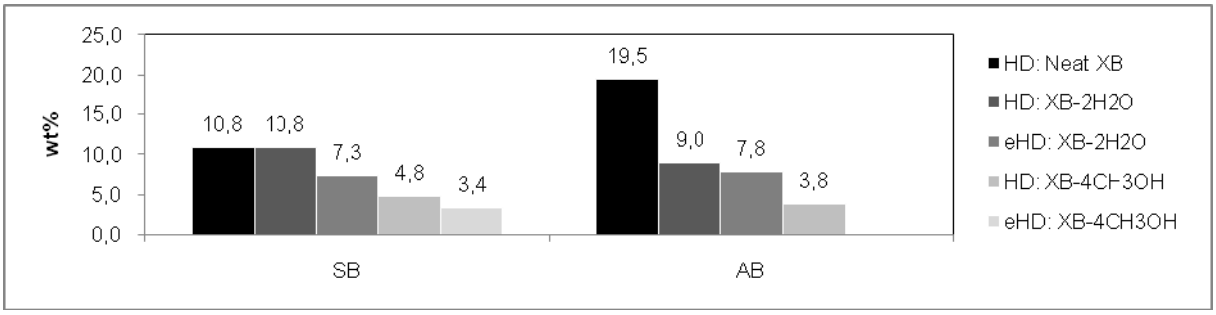

Figure 4: HDs and eHDs of neat XB (with X = S or A), XB-2H_2O and XB-4CH_3OH systems (the determination of the eHD of AB-4CH_3OH has been discarded because of a low HD, i.e. 3.8 wt%).

4 Outlook and Conclusion

None of the routes discussed heretofore can be envisaged for automotive applications but this is not the case for the thermolysis of AB. The thermolysis of AB is a simple reaction to implement for releasing stored hydrogen but in the meantime it is the most difficult to chemically achieve [3]. The 1st equiv. H_2 is generated at temperatures up to 120 °C (Figures 1 and 5). It can also be released at 85 °C after 17 h [40]. The 2nd equiv. H_2 is released at < 200 °C (Figure 5) and the 3rd one at temperatures up to 500 °C [12]. Such releasing rate is unacceptable for applications and to improve it several solutions (dispersion of AB in ionic liquid [43] or solvent [41], its incorporation into a nanoporous scaffold [42], catalysis [44,43]) have been considered. The objective is simply to decrease the dehydrogenation temperatures of the 2 equiv. H_2 (corresponding to an eHD of 13.0 wt%) towards 85 °C (Figure 5), which is the target set by the US DOE [4]. According to Stephens et al. [44], a rapid rate and acceptable extent of dehydrogenation have not been achieved yet, even despite a catalyst. Be that as it may, the AB thermolysis is the route having the highest potential for on-board hydrogen storage for automotive applications.

Neither SB nor AB are mature enough to envisaging technological applications. Both suffer from various issues [3]: catalyst inefficiency in terms of durability in the cases of the SB and AB hydrolysis; low, but not-optimised, eHDs in all cases; and too low hydrogen generation rates for the AB thermolysis. There are many other issues [5, 47, 45, 46]. One of the most significant ones, which has not been discussed yet, is related to the storage irreversibility, that is, the inefficiency in spent fuel recycling (off-board process). Other examples are the purity of generated H_2 (i.e. presence of gaseous by-products such as B_2H_6 [12] in the gas stream from the AB thermolysis or NH_3 released during the AB hydrolysis), the borates crystallisation in the case of the hydrolysis, the thermal management, especially in the case of SB hydrolysis, and so on.

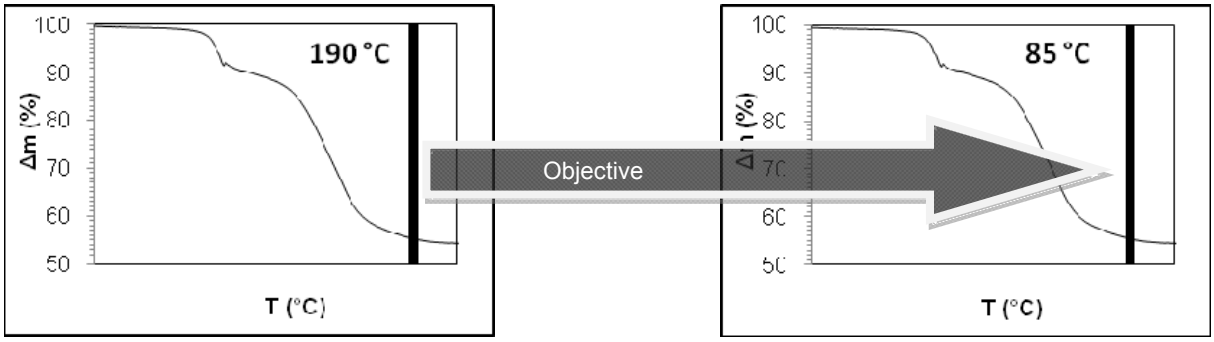

Figure 5: Thermolysis of AB: the objective is to release 2 equiv. H_2 at temperatures up to 85 °C.

SB is not really competing with AB and each may be intended to specific applications [3]. The SB hydrolysis has a higher potential for portable applications owing to its eHDs, commercial availability, and cost while the AB thermolysis has the highest potential for automotive applications owing to high eHDs and a real potential of improvement [47].

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